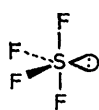


## Ab initio SCF-MO Study of the Reaction Intermediates formed by Addition of Thiohypochlorous Acid to Ethylene

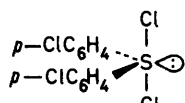
By Valeria M. Csizmadia, George H. Schmid, Paul G. Mezey, and Imre G. Csizmadia,\* Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Non-empirical SCF-MO calculations, using two different basis sets, were carried out on a cyclic sulphurane and a thiiranium-chloride ion-pair. The calculated energies indicated that in the gas phase the covalent cyclic sulphurane is favoured over the ionic species. The activation energy for the internal collapse of the cyclic sulphurane to product was calculated to be 42 kcal mol<sup>-1</sup>, well below the energy of the thiiranium-chloride ion-pair. These results support the suggestion that thiiranium ions prevail in polar solvents but tetravalent sulphur intermediates are favoured in solvents of low polarity.

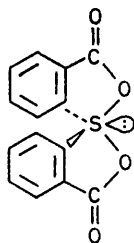
It is well known that sulphur can form tetravalent compounds [*e.g.* (1)] with highly electronegative elements.<sup>1</sup> Recently a number of compounds containing a tetravalent sulphur atom with one or more organic ligands [*e.g.* (2) and (3)] have been prepared.<sup>2</sup> The



(1)



(2)



(3)

structure of these compounds is a slightly distorted trigonal bipyramid with the unshared pair of electrons occupying the equatorial and the most electronegative atoms occupying the axial positions.

The intermediacy of tetravalent sulphur compounds has been proposed in a number of reactions.<sup>3</sup> Among

<sup>1</sup> W. C. Smith, *Angew. Chem.*, 1962, **74**, 742.

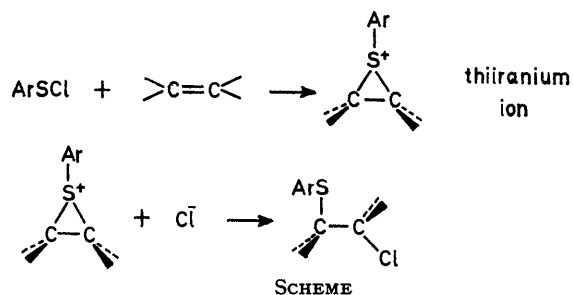
<sup>2</sup> (a) N. Baenziger, R. Buckles, R. Maner, and T. Simpson, *J. Amer. Chem. Soc.*, 1969, **91**, 5749; (b) I. Kapovits and A. Kalman, *Chem. Comm.*, 1971, 649.

<sup>3</sup> N. E. Hester, *Internat. J. Sulfur Chem.*, 1973, **8**, 119.

<sup>4</sup> N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, 1949, **71**, 2724.

<sup>5</sup> C. Brown and D. R. Hogg, *Chem. Comm.*, 1966, 138.

these is the addition of arenesulphenyl halides to alkenes. The original mechanism proposed by Kharasch<sup>4</sup> is shown in the Scheme. This mechanism, which involves



a thiiranium ion intermediate and two transition states, was proposed in order to explain the highly stereospecific *anti*-addition, yielding different products from *cis*- and *trans*-olefins. Nevertheless, recent data on the influence of substituents both in the sulphenyl chloride<sup>5</sup> and alkene<sup>6-8</sup> and the nature of the effects of solvents and temperature<sup>9</sup> do not exclude the possibility of other cyclic intermediates.

<sup>6</sup> G. H. Schmid and D. G. Garratt, *Canad. J. Chem.*, 1973, **51**, 2463.

<sup>7</sup> G. H. Schmid and D. G. Garratt, *Canad. J. Chem.*, 1974, **52**, 1807.

<sup>8</sup> G. H. Schmid and V. J. Nowlan, *Canad. J. Chem.*, 1976, **54**, 695.

<sup>9</sup> G. H. Schmid and V. M. Csizmadia, *Canad. J. Chem.*, 1972, **50**, 2465.

If the reaction of sulphenyl chloride with alkenes is regarded as a nucleophilic substitution reaction at sulphur instead of the usual electrophilic addition, the mechanism proposed by Kharasch is not unique.<sup>10</sup> Two mechanisms which have been proposed for nucleophilic displacement at sulphur are shown in Figure 1.

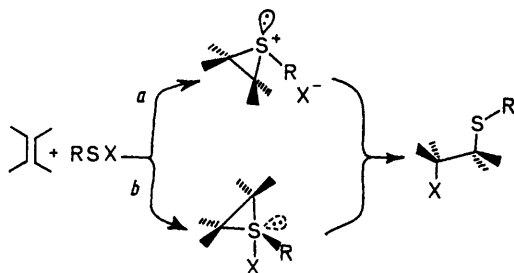
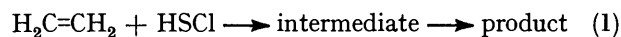


FIGURE 1 Possible reaction mechanisms for sulphenyl halide addition to olefins

Path *a* which is the sulphur analogue of the  $S_N2$  mechanism leads to a single intermediate and is identical with the Kharasch mechanism. Path *b* involves formation of a tetravalent sulphur intermediate which may ionize to the thiiranium ion or may collapse internally to products. Evidence for a distinct tetravalent sulphur intermediate has been claimed.<sup>11</sup>

Owing to this current interest in tetravalent sulphur species, this study was undertaken in order to obtain a theoretical insight into the relative stabilities of the two possible reaction intermediates of the addition reaction of a sulphenyl chloride to an alkene: a covalent sulphurane and a thiiranium-chloride ion-pair.

In order to reduce the size of the various species and to eliminate the need to optimize the geometry of substituents, our theoretical studies were carried out on the reaction of ethylene and thiohypochlorous acid HSCl.



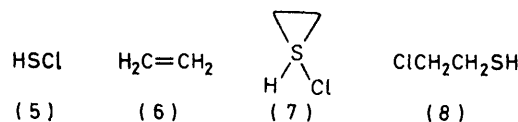
#### METHOD

The non-empirical or Hartree-Fock type LCAO-SCF-MO calculations were carried out on an IBM 370/165 computer using the Gaussian 70 program system.<sup>12</sup> A 4-31 G split valence shell basis set was used throughout this study,<sup>13</sup> though for comparisons with previous results 3G minimum basis<sup>12</sup> calculations were also performed. The geometries of the structures were systematically optimized in three series of sequential optimizations involving all geometrical parameters.

#### RESULTS AND DISCUSSION

The structural parameters for the optimum geometries of all four species (5)–(8) are listed in Tables 1 and 2. In addition the geometries of selected points on the potential energy surface of the cyclic  $\rightarrow$  open reaction, representing an arbitrarily chosen reaction path, are

also given in Table 3. The optimum conformations of the cyclic sulphurane (7) and the open structure (8) are shown on Figures 2 and 3.



The configuration about the sulphur atom in the sulphurane (7) is an approximate trigonal bipyramid. The S-C bond of the three-membered ring and the hydrogen occupy two of the equatorial positions with the HSC angle between them being  $95.40^\circ$ . The third

TABLE 1

Optimum geometries of HSCl and  $\text{H}_2\text{C}=\text{CH}_2$

Structural parameter	HSCl	$\text{H}_2\text{C}=\text{CH}_2$
H-S (Å)	1.357 0	
S-Cl (Å)	2.166 6	
$\widehat{\text{HSC}}$ (°)	94.98	
H-C (Å)	1.074	1.074 3
C-C (Å)		1.320 2
$\widehat{\text{HCC}}$ (°)		121.95

TABLE 2

Optimum geometries<sup>a</sup> of cyclic  $[\text{CH}_2]_2\text{SCIH}$  (7) and open  $\text{ClCH}_2\text{CH}_2\text{SH}$  (8)

Structural parameter <sup>b</sup>	(7)	(8)
H(1)S(2)	1.339 6	1.329 9
S(2)C(3)	1.939 7	1.806 5
S(2)C(4)	1.844 7	
C(3)C(4)	1.490 3	1.541 7
S(2)Cl(5)	2.465 5	
C(4)Cl(5)		1.813 8
C(4)H(6)	1.087 1	1.090 9
C(4)H(7)	1.086 9	1.090 9
C(3)H(8)	1.081 1	1.088 6
C(3)H(9)	1.080 7	1.088 6
H(1)S(2)Cl(5)	78.95	
H(1)S(2)C(3)	90.05	94.58
H(1)S(2)C(4)	95.40	
C(3)S(2)Cl(5)	156.17	
C(3)C(4)Cl(5)		112.28
C(4)S(2)Cl(5)	113.24	
Cl(5)C(4)H(6)		106.81
C(3)S(2)C(4)	46.30	
Cl(5)C(4)H(7)		106.81
S(2)C(3)C(4)	63.49	108.73
S(2)C(4)C(3)	70.21	
C(3)C(4)H(6)	120.66	110.93
C(3)C(4)H(7)	118.27	110.93
C(4)C(3)H(8)	117.93	109.28
C(4)C(3)H(9)	117.03	109.28
H(6)C(4)H(7)	114.22	108.88
H(8)C(3)H(9)	115.65	107.41
H(1)S(2)C(3)C(4)	97.44	180.00
S(2)C(3)C(4)H(6)	106.44	60.57
S(2)C(3)H(4)Cl(5)		180.00
H(6)C(4)C(3)H(9)	146.87	178.06

<sup>a</sup> For the numbering of atoms see also Figures 2 and 3.

<sup>b</sup> Symbols XY, XYZ, and XYZW stand for bond length (Å), bond angle (°), and dihedral angle (°), respectively.

equatorial position is considered to be taken by the lone pair of electrons. The apical positions are occupied by

<sup>10</sup> G. H. Schmid and D. G. Garratt in 'Double-bonded Functional Groups,' Supp. Vol. 1, ed. S. Patai, Wiley, London, 1976, ch. 9.

<sup>11</sup> D. C. Ousley, G. K. Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, 1969, **91**, 5239.

<sup>12</sup> W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, Quantum Chemistry Program No. 236, Indiana University, Bloomington, Indiana.

<sup>13</sup> R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.

the electronegative chlorine and the second S-C bond of the ring. The  $\widehat{\text{CSCl}}$  (axial) angle is  $156.17^\circ$  with the distortion from linearity in the direction of the equatorial S-C and S-H bonds and away from the lone pair. The rather significant deviation from an ideal trigonal bipyramid structure is due mainly to the presence of the

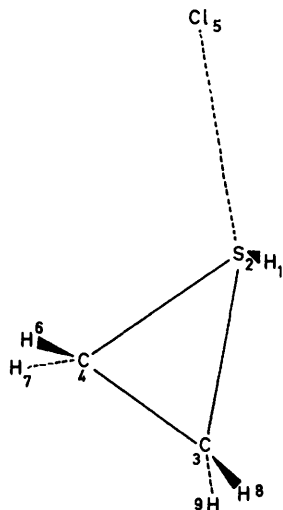


FIGURE 2 Optimum structure of cyclic sulphurane (7)

three-membered ring. However, the interaction between the lone pairs on sulphur and chlorine also contributes to the distortion of the geometry. It is of some interest, that the C-C bond length ( $1.4903 \text{ \AA}$ ) in the cyclic sulphurane is significantly shorter than in the open

to assume larger values in the constrained ring. However, the optimum  $63.49$  and  $70.21^\circ$  values for the two  $\widehat{\text{SCC}}$  angles are still rather far from the ideal tetrahedral angles (deviations are  $45.97$  and  $39.25^\circ$ , respectively). Consequently, the hybridization state of the

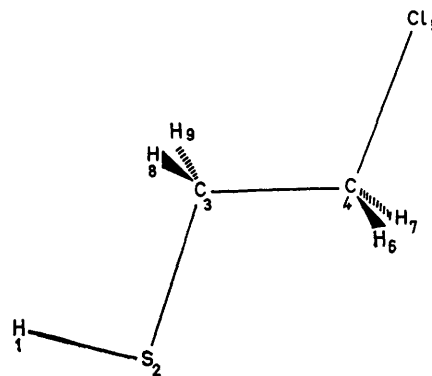


FIGURE 3 Optimum structure of addition product (8)

two carbon atoms as may be judged from the molecular geometry is rather different from the ideal  $sp^3$ , and this deviation may contribute to the C-C bond shortening mentioned above. The  $\widehat{\text{CSC}}$  bond angle distortion of  $43.70^\circ$  is comparable to the other two ring-angle distortions, though in relative scale it is more significant as it represents almost 50% decrease (the angle is  $46.30$  instead of the ideal  $90^\circ$ ). This easy deformability of the sulphur system is analogous to the conformational 'flexibility' of sulphimides found in earlier theoretical studies.<sup>14-16</sup>

TABLE 3

Geometries and (3G) total energies of intermediate structures along an assumed reaction path for the cyclic structure  $\rightarrow$  open structure conversion

Atom	Cyclic structure			First intermediate A (25% conv.)			Co-ordinates ( $\text{\AA}$ ) Second intermediate B (50% conv.)			Third intermediate C (75% conv.)			Open structure		
	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z
H(1)	-0.779 3	-1.814 1	-1.328 3	-1.360 0	-1.960 0	-1.160 0	-2.400 0	-1.910 0	-0.862 0	-3.030 0	-1.710 0	-0.458 0	-3.411 2	-1.385 7	0.0
S(2)	-0.624 5	-1.735 8	0.0	-0.990 0	-1.900 0	0.0	-1.370 0	-1.910 0	0.0	-1.750 0	-1.850 0	0.0	-2.121 7	-1.710 9	0.0
C(3)	-1.490 3	0.0	0.0	-1.503 0	0.0	0.0	-1.516 0	0.0	0.0	-1.528 8	0.0	0.0	-1.541 7	0.0	0.0
C(4)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cl(5)	1.106 7	-3.392 5	-0.580 3	1.980 0	-2.490 0	-0.435 0	2.340 0	-1.100 0	-0.290 0	1.950 0	0.420 0	-0.145 0	0.687 7	1.678 4	0.0
H(6)	0.544 3	0.264 6	-0.896 9	0.630 0	0.060 0	-0.894 5	0.650 0	-0.150 0	-0.892 1	0.555 0	-0.345 0	-0.889 2	0.389 7	-0.500 6	-0.887 4
H(7)	0.514 7	0.235 2	0.927 8	0.600 0	0.050 0	0.917 7	0.640 0	-0.150 0	0.907 6	0.550 0	-0.345 0	0.897 5	0.389 7	-0.500 6	0.887 4
H(8)	-1.996 7	0.298 2	-0.907 4	-1.980 0	0.370 0	-0.899 9	-1.96 00	0.430 0	-0.892 4	-1.935 0	0.480 0	-0.894 9	-1.901 1	0.534 8	-0.877 4
H(9)	-1.981 4	0.276 5	0.922 1	-1.970 0	0.350 0	0.910 1	-1.950 0	0.420 0	0.899 8	-1.930 0	0.475 0	0.888 6	-1.901 1	0.534 8	0.877 4
Total energy (a.u.)	-925.312 77			-925.245 60			-925.248 97			-925.260 76			-925.475 10		

structure ( $1.5417 \text{ \AA}$ ), in spite of the fact that the former bond spans the distance between a formally 'apical' and an 'equatorial' position.

The positional differences between the two carbon atoms are reflected in the different S-C bond lengths; the 'apical' S-C bond length is  $1.9397 \text{ \AA}$  while the 'equatorial' S-C bond length is  $1.8447 \text{ \AA}$ , in agreement with the general characteristics of molecules of trigonal bipyramid structure. The  $\widehat{\text{CSC}}$  angle is unusually small, merely  $46.30^\circ$ , which allows the two  $\widehat{\text{SCC}}$  angles

The optimum conformation of the open addition product structure (8) has a plane of symmetry containing atoms H-S-C-C-Cl in an antiperiplanar arrangement. As the constraints imposed by the ring are removed, all bond lengths and angles have values that do not deviate much from those most commonly observed.

The calculated total energies are given in Table 4. The second step of reaction (1) may also be studied in terms of a possible ion-pair recombination reaction of the type (2). For the sake of comparison the STO 3G results on reactions (3) and (4) have also been calculated

<sup>14</sup> P. Mezey and A. Kucsman, *Chem. Comm.*, 1971, 1448.

<sup>15</sup> P. Mezey and A. Kucsman, *J.C.S. Faraday II*, 1972, 2060.

<sup>16</sup> P. Mezey, A. Kalman, and A. Kucsman, *Internat. J. Sulfur Chem. A*, 1972, 2, 187.

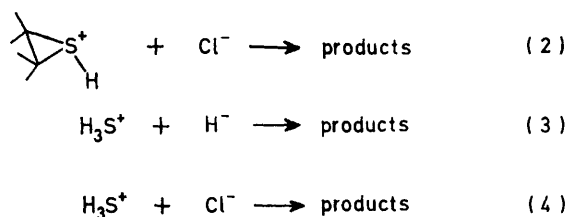
and included in Table 4 together with the corresponding STO 3G energies for reaction (2).

In Figure 4 the calculated results for reactions (2)—(4) are shown. The calculated total energies indicate

TABLE 4		
Calculated total energies (a.u.) of optimum structures		
Structure	STO 3G	STO 4-31G
	-77.073 96	-77.922 13
HSCl	-848.322 29	-856.603 69
Cl <sup>-</sup>	-454.480 42	-459.026 48
	-470.663 83	-475.271 89
	-925.312 77	-934.443 605
	-925.475 10	-934.564 14
H <sub>2</sub> S	-394.311 63	
HCl	-455.136 01	
H <sub>2</sub>	-1.117 54	
H <sub>3</sub> Scl	-849.333 18	
H <sub>3</sub> S <sup>+</sup>	-394.666 72	
H <sub>4</sub> S (ref.17)	-395.147 62	

that in the gas phase the covalent species are favoured over the ionic species. The stability of the sulphurane products relative to that of the covalent decomposition products shows consistent improvement as the central sulphur becomes more heavily substituted.

The calculated relative thermodynamic stabilities of



various species in reaction (1) are shown in Figure 5. Both STO 3G and STO 4-31G results give the same qualitative conclusions of the relative stabilities of the intermediates: the cyclic structure is >90 kcal mol<sup>-1</sup> more stable than the ion-pair. In order to rule out the ion-pair as the intermediate in a gas-phase reaction, however, one should also consider potential barriers in the formation and rearrangement reactions of the

<sup>17</sup> G. M. Schwenzer and H. F. Schaefer III, *J. Amer. Chem. Soc.*, 1975, **97**, 1393.

cyclic intermediate (7). The formation of the cyclic structure (7) is assumed to require only slightly >53 kcal mol<sup>-1</sup> activation energy. On the other hand, the

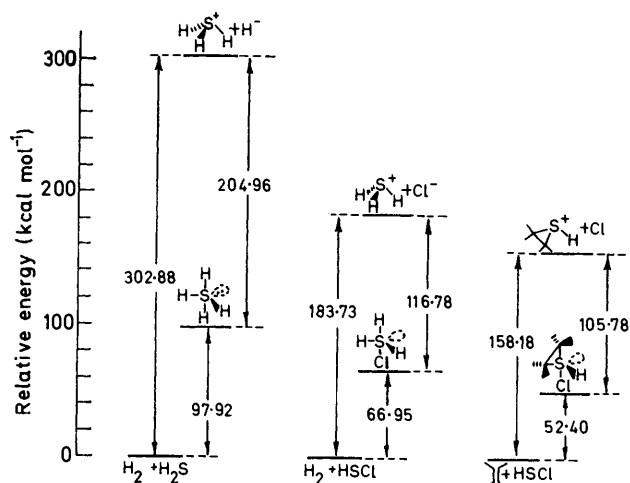


FIGURE 4 Calculated energy differences in various ion-pair rearrangement reactions (calculated with STO 3G bases)

rearrangement reaction of (7) leading to structure (8) is likely to pass through the highest point of the entire reaction path, as this reaction requires breaking of  $\sigma$  bonds.

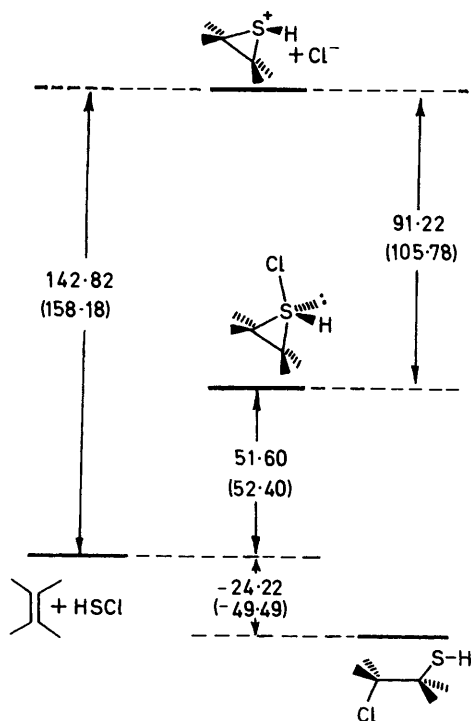


FIGURE 5 Calculated relative stabilities of reactants, intermediates, and products in thiohypochlorous acid and olefin addition reaction. Given are STO 4-31G and STO 3G energy values (latter in parentheses) in kcal mol<sup>-1</sup> relative to the H<sub>2</sub>C=CH<sub>2</sub> + HSCl system

Since this internal collapse of sulphurane to the addition product is of considerable interest, we have calculated the energies of three additional structures

along a hypothetical reaction path. These structures were derived by assuming an arbitrary but plausible path for the motion of the chlorine atom and by taking

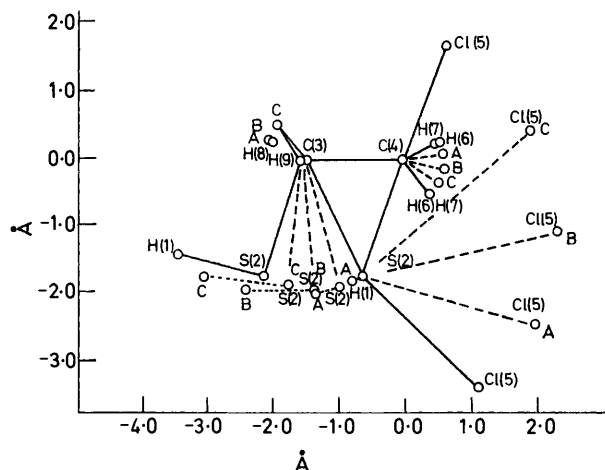


FIGURE 6 Assumed rearrangement scheme for the cyclic sulphurane  $\rightarrow$  open addition product reaction. Symbols A—C show the relative positions of atoms in intermediates A—C (see Table 3) respectively

appropriate (3:1, 1:1, 1:3) linear combinations of the remaining internal co-ordinates, formally representing 25, 50, and 75% interconversion of (7) to (8). The

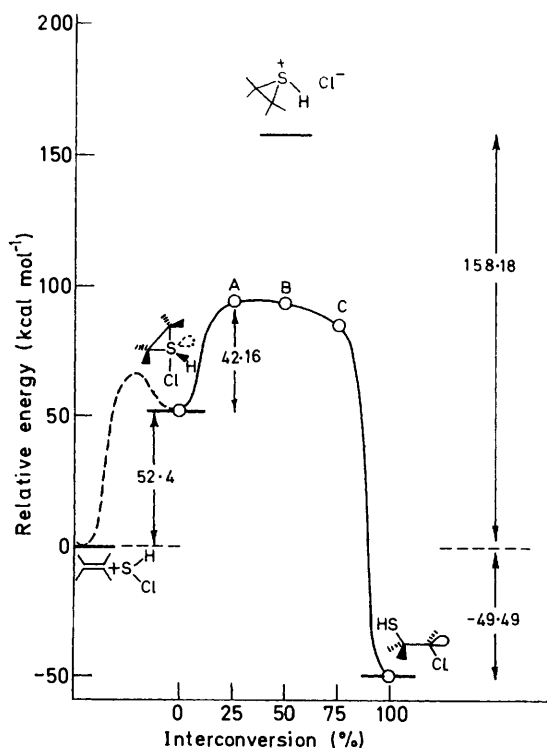


FIGURE 7 Calculated energy variation along the assumed reaction path

geometries of these structures are specified and their calculated total energies are given in Table 3, the rearrangement of the atoms is shown on Figure 6.

The calculated total energies indicate that this particular reaction path requires an activation energy of *ca.* 42 kcal mol<sup>-1</sup>, *i.e.* the entire path runs much below the energy of the (CH<sub>2</sub>)<sub>2</sub>SH<sup>+</sup> + Cl<sup>-</sup> ion-pair (see Figure 7). Since the reaction path itself is by no means optimized, it is very likely that the true reaction path requires an activation energy considerably <42 kcal mol<sup>-1</sup>.

The calculated charges on the atoms during the rearrangement are shown on Figure 8. Though charge distributions calculated with small basis sets should be interpreted with proper caution, it is remarkable that the charge separation in the covalent intermediate is rather large. This indicates, that in appropriate polar solvent the formally covalent compound would be solvated to a degree comparable to that of the ion-pair, since the chlorine atom has assumed 75% of the full negative charge.

Along the assumed reaction co-ordinate at 25% interconversion the negative charge of the chlorine is 95% of a

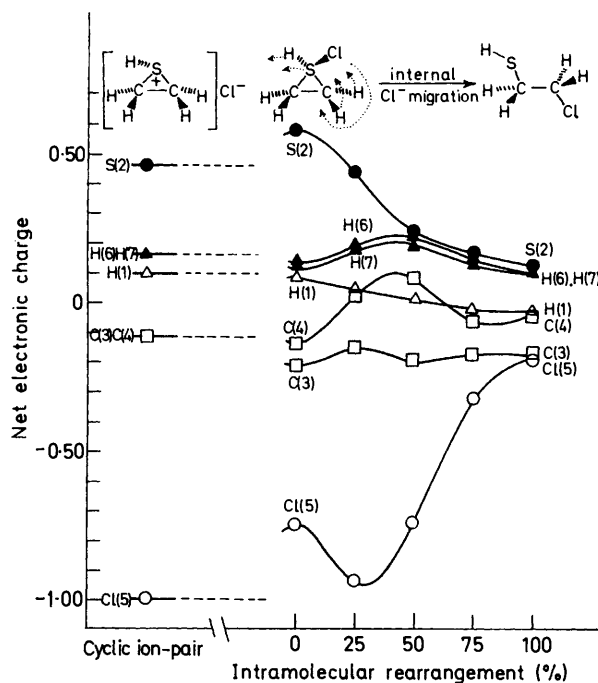


FIGURE 8 Calculated changes in charge distribution along the assumed reaction path

full charge even though the geometric change is relatively small, dominated by an S—Cl 'bond stretching'. This may be interpreted by assuming that *ca.* 25% along the reaction co-ordinate we have a structure that resembles an 'intimate ion-pair'. From 25% onward the charge distribution converges to that of the covalent addition product.

In conclusion, we might say that the energetics of these calculations clearly indicate that at least in the gas phase the internal collapse is favoured over the separated ion-pair mechanism. On the other hand, the computed charge distribution indicates that the solvation along the internal collapse should not be all that different

from the solvation of the separated ion-pair. Consequently, if the reaction conditions (solvent, temperature, concentration, *etc.*) are appropriately chosen both mechanisms may be operative in solution. This is in accord with the suggestion of Helmkamp<sup>11</sup> and Zefirov,<sup>18</sup> that the thiiranium salt prevails in solvents of high

polarity which can solvate the halide ions well but tight ion pairs or tetravalent sulphur intermediates are favoured in solvents of low polarity.

[6/1243 Received, 28th June, 1976]

<sup>18</sup> I. V. Bodrikov, T. S. Ganghenko, and N. S. Zefirov, *Doklady Akad. Nauk S.S.S.R.*, 1976, **226**, 831.

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